Module 6 – Green Chemistry in the Real World II

Global Greenchem Innovation & Network Program

UNIDO

Green Chemistry Toolkit

gef

Center for Green Chemistry & Green Engineering at Yale

Companies that do Green Chemistry!

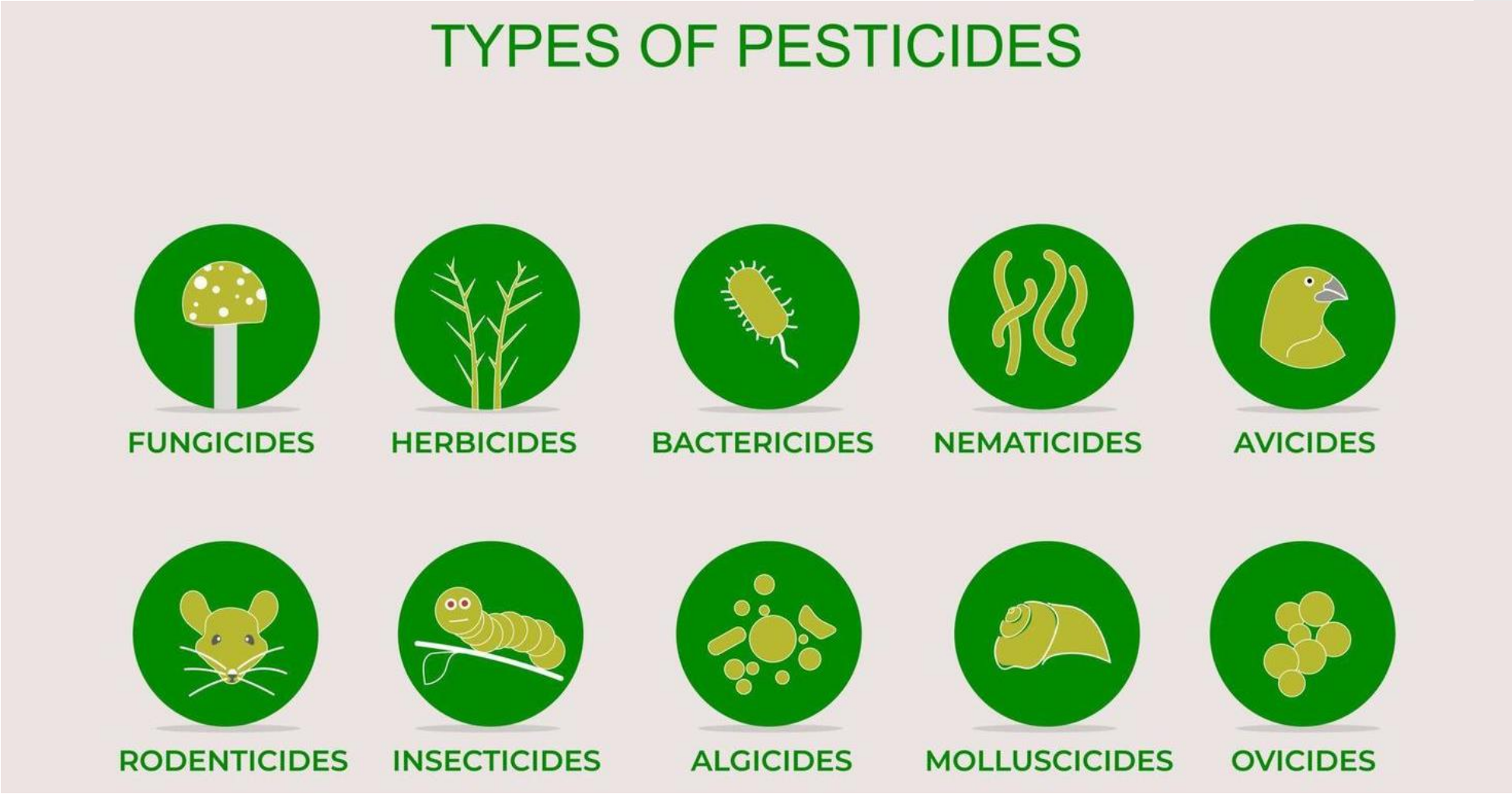
Provivi

Why do we need pesticides?


Credit: Wikimedia

- Pesticides of many different kinds are important for global food security.
- Pests of different kinds affect almost all staple foods around the world.

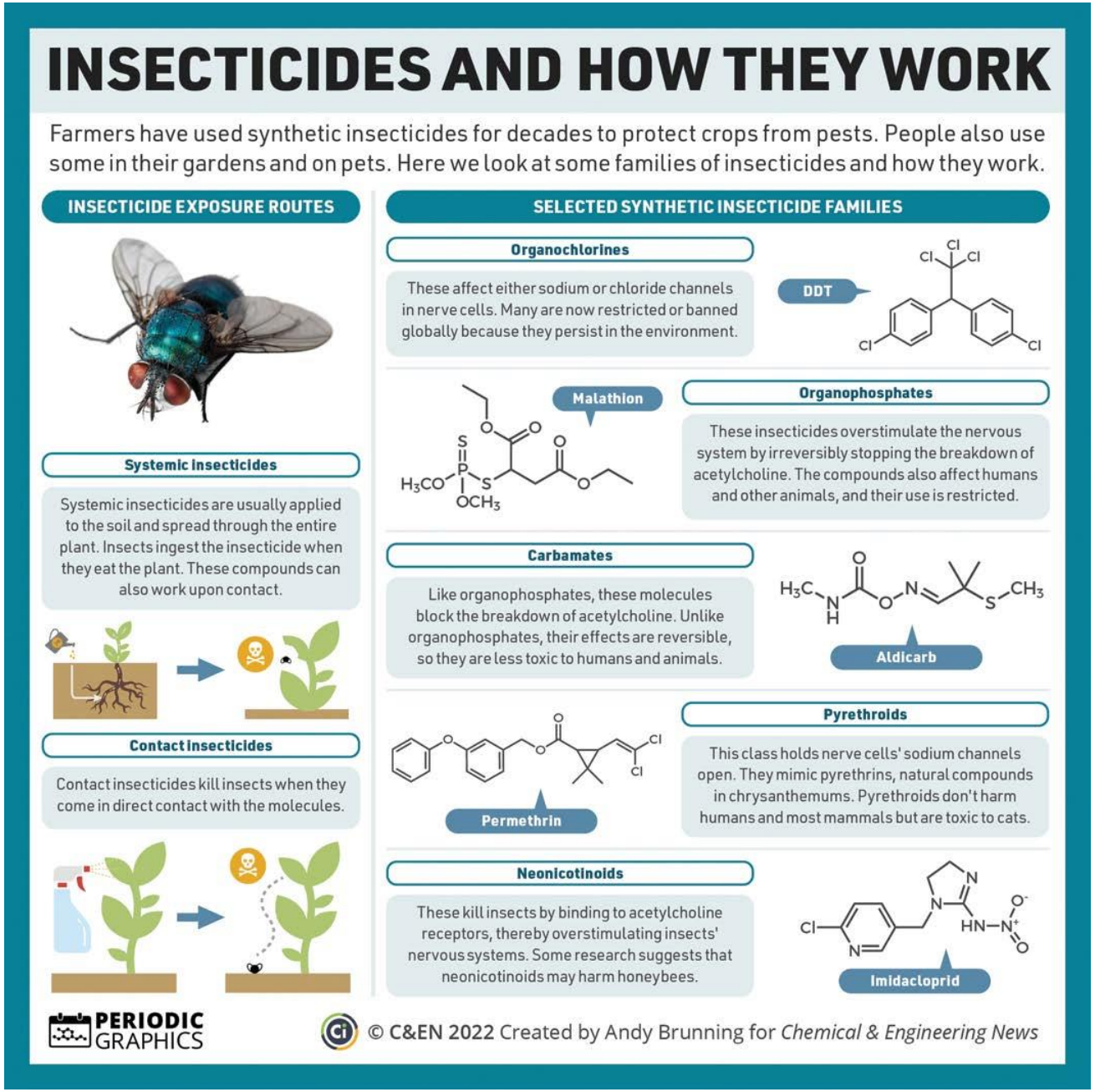
What kind of pesticides are there?



https://www.vecteezy.com/vector-art/11512357-types-of-pesticides-include-herbicides-insecticides-fungicides-molluscicides-plant-protections-in-agriculture

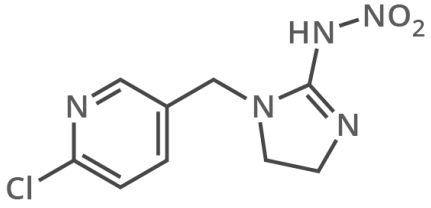
Insecticides

- Insecticides are the kind of pesticides specialized to control the effects of insects.

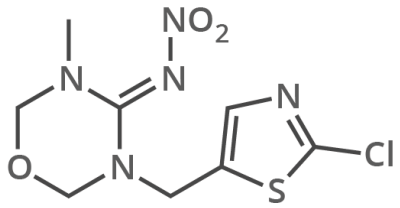


NEONICOTINOID PESTICIDES - THE FACTS

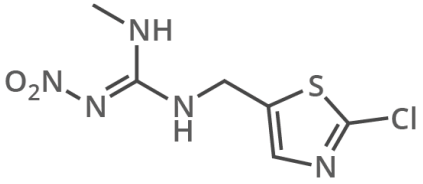
The use of neonicotinoid pesticides has been a contentious issue in recent years. They account for around 25% of the global agrochemical market, but have also been linked with negative environmental effects. This graphic looks at how they work, and the nature of the concerns surrounding them.



IMIDACLOPRID



THIAMETHOXAM



CLOTHIANIDIN

1980s Decade in which neonicotinoid pesticides first developed

120 Number of countries in which neonicotinoids are registered

1 Now used more than any other class of insecticide.

HOW DO NEONICOTINOIDS WORK?

Can be added to irrigation water, then taken up & spread through plant tissues. Also used in seed treatments.

Bind to nicotinic receptors for the neurotransmitter acetylcholine in the insect central nervous system.

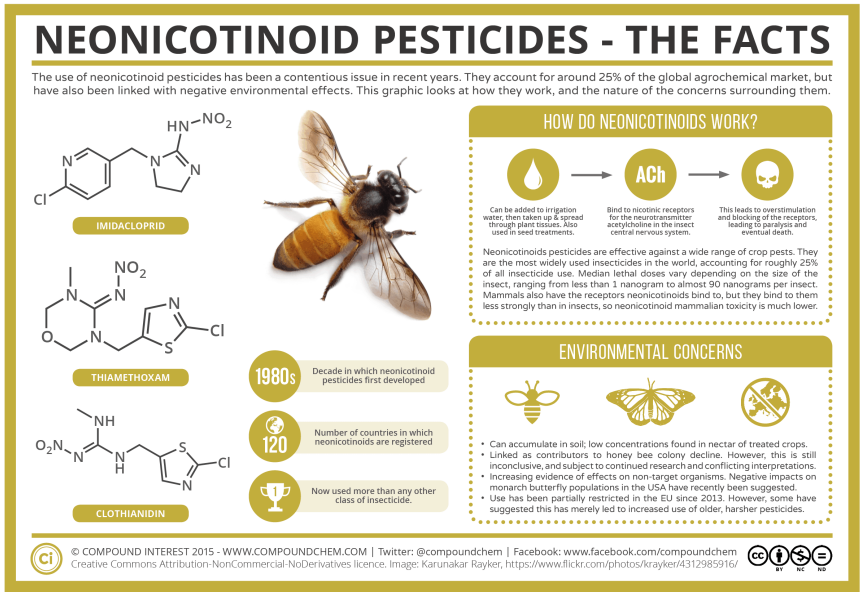
This leads to overstimulation and blocking of the receptors, leading to paralysis and eventual death.

Neonicotinoids pesticides are effective against a wide range of crop pests. They are the most widely used insecticides in the world, accounting for roughly 25% of all insecticide use. Median lethal doses vary depending on the size of the insect, ranging from less than 1 nanogram to almost 90 nanograms per insect. Mammals also have the receptors neonicotinoids bind to, but they bind to them less strongly than in insects, so neonicotinoid mammalian toxicity is much lower.

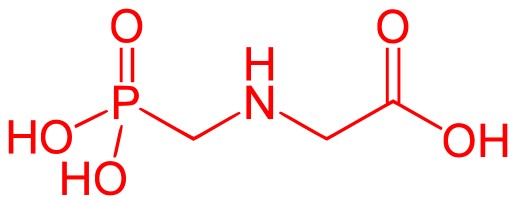
ENVIRONMENTAL CONCERNS

- Can accumulate in soil; low concentrations found in nectar of treated crops.
- Linked as contributors to honey bee colony decline. However, this is still inconclusive, and subject to continued research and conflicting interpretations.
- Increasing evidence of effects on non-target organisms. Negative impacts on monarch butterfly populations in the USA have recently been suggested.
- Use has been partially restricted in the EU since 2013. However, some have suggested this has merely led to increased use of older, harsher pesticides.

Neonicotinoids are broadband Insecticides



- While Neonicotinoids are broadspectrum insecticides, glyphosate is a broadspectrum herbicide (Round-Up).

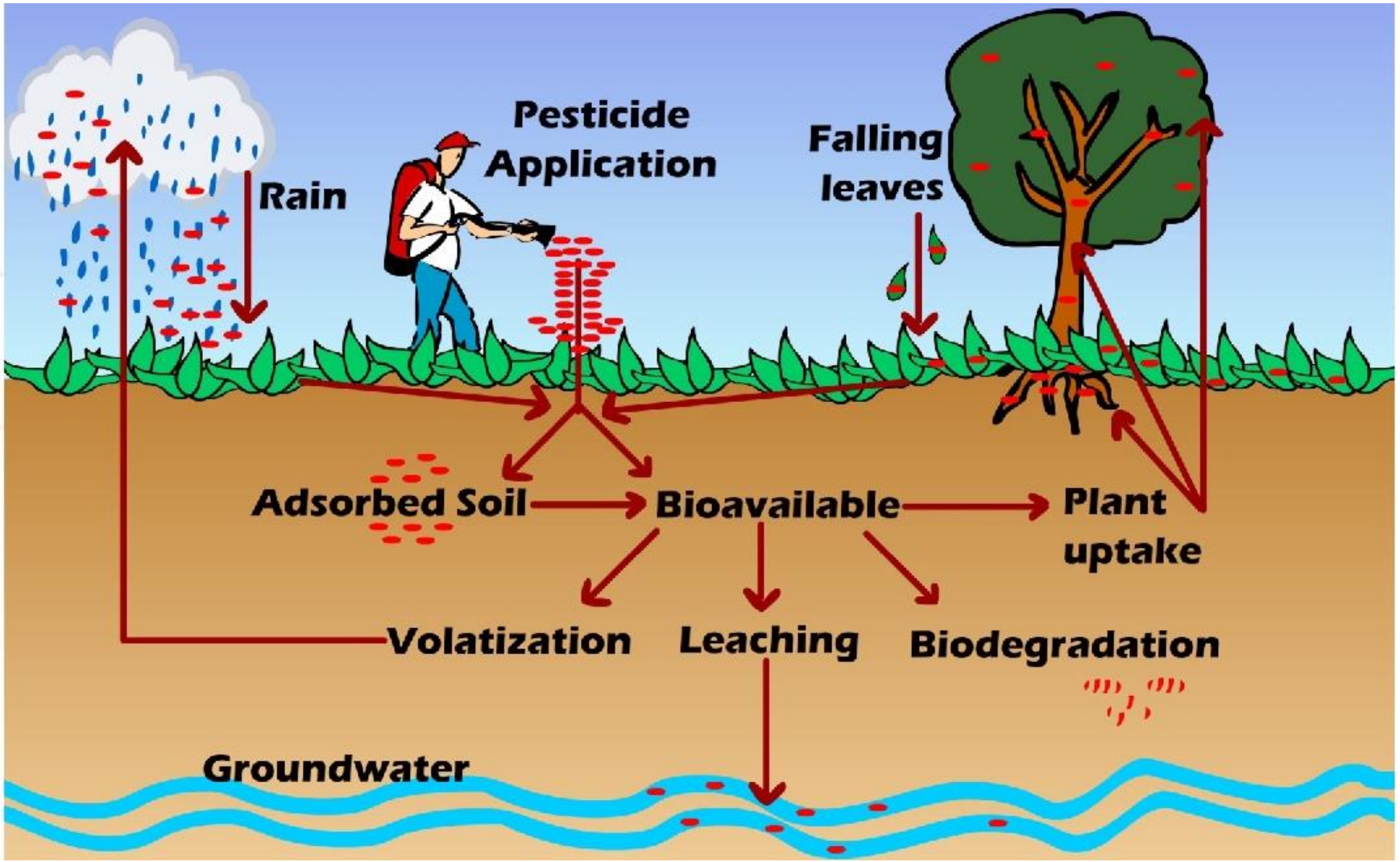


Pesticides and broadband, a big problem

- Pesticides that are broadly acting and are persistent are a special harm for entire ecosystems.
- Bee populations are suffering due to the widespread use of different pesticides (not only insecticides).

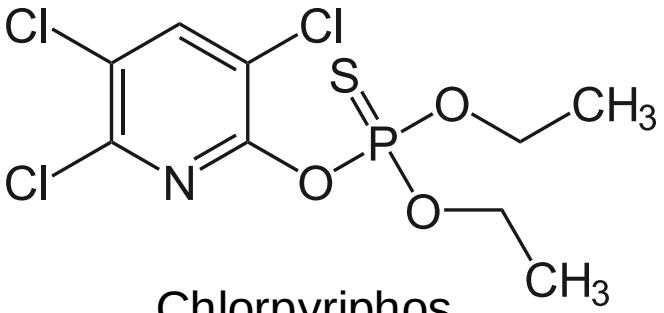
Modern pesticides are developed with a focus on highly **specific activity**, **low toxicities**, and **good degradability**.

Persistent pesticides are a real problem

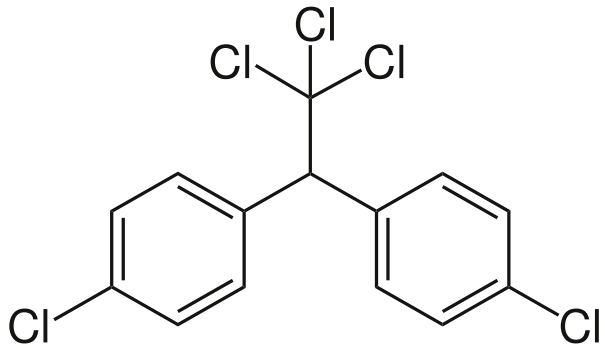


Langenbach, Tomaz. "Persistence and Bioaccumulation of Persistent Organic Pollutants (POPs)." (2013).

Persistent pesticides are a real problem



Chlorpyriphos



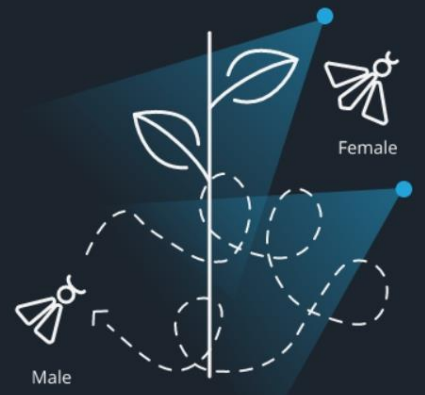
DDT

- Since pesticides are usually applied in vast areas, it is especially problematic if they are persistent and do not biodegrade easily.
- DDT and Chlorpyriphos are only two examples of persistent insecticides, so called Persistent Organic Pollutants (POPs).

Provivi's Approach

Pheromones

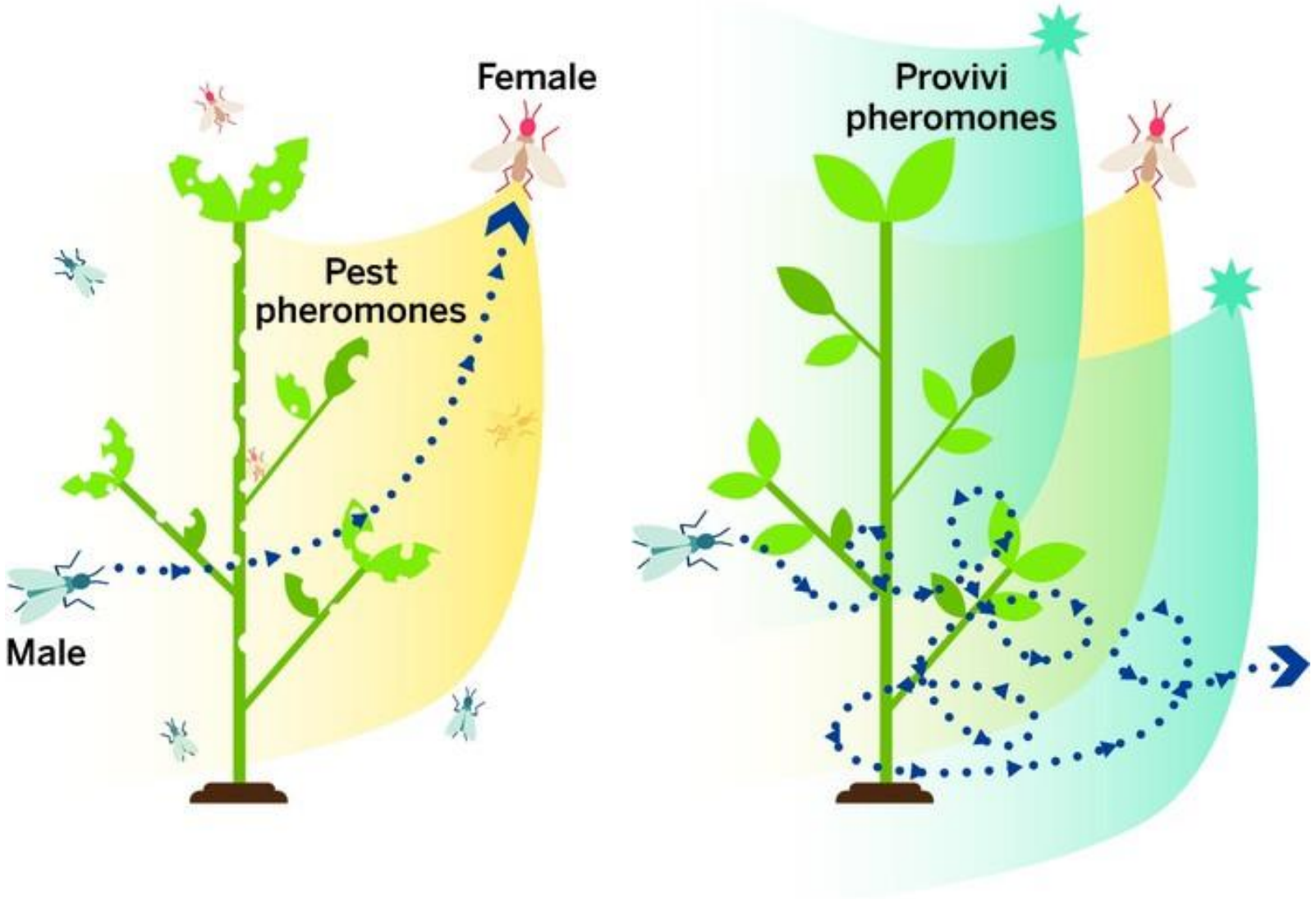
Insects produce pheromones to communicate with other insects, helping them mate, find food, and escape predators. Female insects usually release sex pheromones to attract a male for mating.



Synthetic Pheromones

By saturating an environment with artificially synthesized female sex pheromones, male insects are unable to find female insects, thus disrupting the mating process.

Provivi's Approach



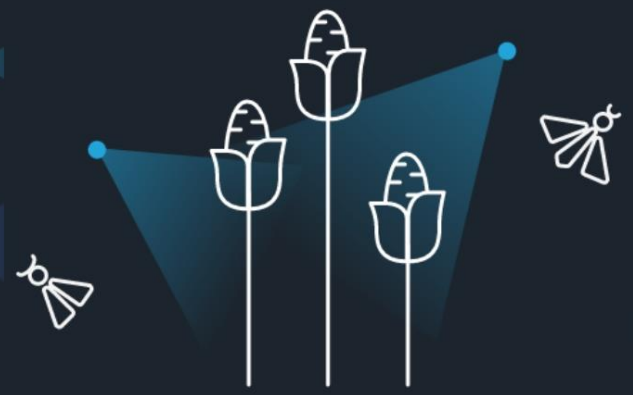
- The synthesis and application of the insect-(pest)-specific pheromone will mislead the male of finding the female insect.

Credit: Provivi

Provivi's Approach

Mating Disruption

Synthesizing pheromones to prevent reproduction is called mating disruption. Unlike traditional insecticides, mating disruption does not kill insects and only results in less offspring in the next generation.



Provivi

One of the biggest limitations to this new technology is high cost. However, Provivi synthesizes pheromones at large scale and reduced cost by using biocatalysts and low-cost raw materials.

Paradigm Shift

Traditionally insecticides have been designed to kill a pest. In this case it is different, since pheromones are applied to disrupt the mating process and keep the population low by diminishing the mating success.

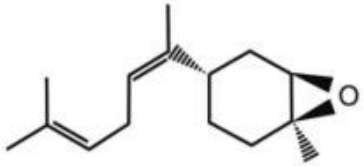
Pheromones

Silkmoth (*Bombyx mori*)
(E,Z)-10-12-hexadecadien-1-ol

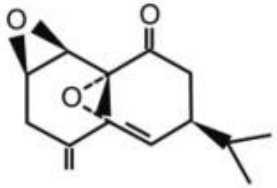
Gypsy moth (*Lymantria dispar*)
Disparlure (+)
(7R,8S)-cis-7,8-Epoxy-2-methyloctadecane

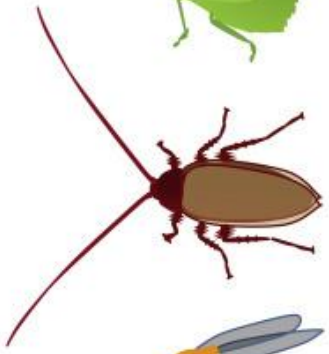
Honeybee (*Apis mellifera*)
(E)-9-oxo-2-decenoic acid

Green stink bug (*Nezara viridula*)
(1S,4S,6R)-1-methyl-4-
((Z)-6-methylhepta-2,5-dien-2-yl)-
7-oxabicyclo[4.1.0]heptane

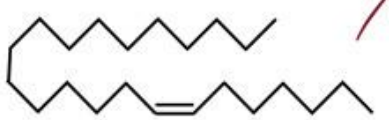


Cockroach (*Periplaneta americana*)
Periplanone B
(1Z,5E)-1,10(14)-diepoxy-4(15),
5-germacradien-9-one





Fruit fly (*Drosophila melanogaster*)
7 tricosene, non volatile

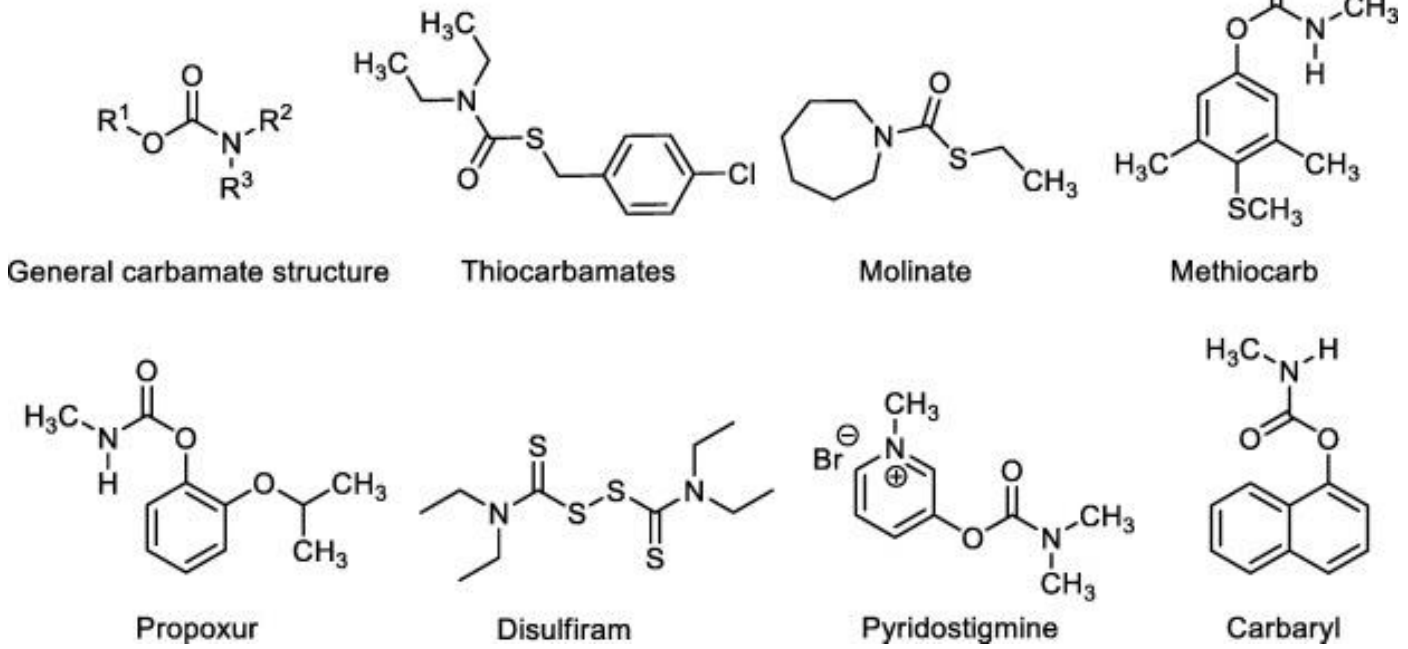


- Since pheromones are biosynthesized by the different organisms they are specified for/by, they are usually environmentally benign, non-persistent, and highly specific (meaning they act at relatively low concentrations, and **only** on the target organism).

Jacquin-Joly, Emmanuelle & Groot, Astrid. (2018). Pheromones, Insects.

Structurally very different

Pesticides are still almost exclusively of synthetic origin and some of them highly toxic, broadband, and structurally different than pheromones.



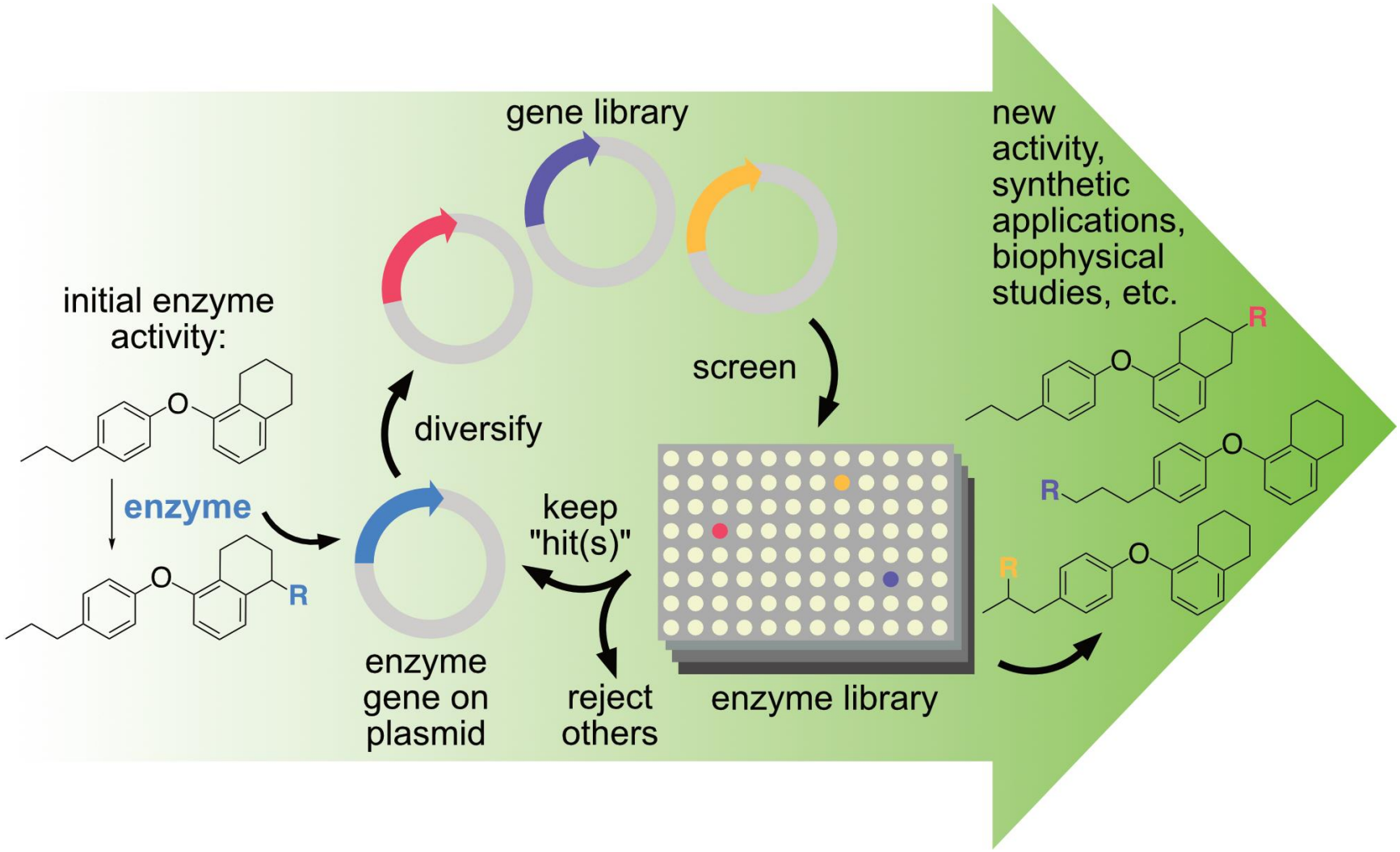
Provivi uses Biocatalysis

- Biocatalysis is the approach that Provivi takes to synthesize their pheromones. They use enzymes that occur in nature (in microorganisms), study promising initial activities for their syntheses and then gradually increase the enzymes activities and selectivities to the desired level. This process is called **directed evolution** and can have a profound impact on the way we 'make' things.

Frances Arnold

- Co-Founder of Provivi
- Nobel Prize in Chemistry 2018 "Directed Evolution of Enzymes"

...and directed Evolution

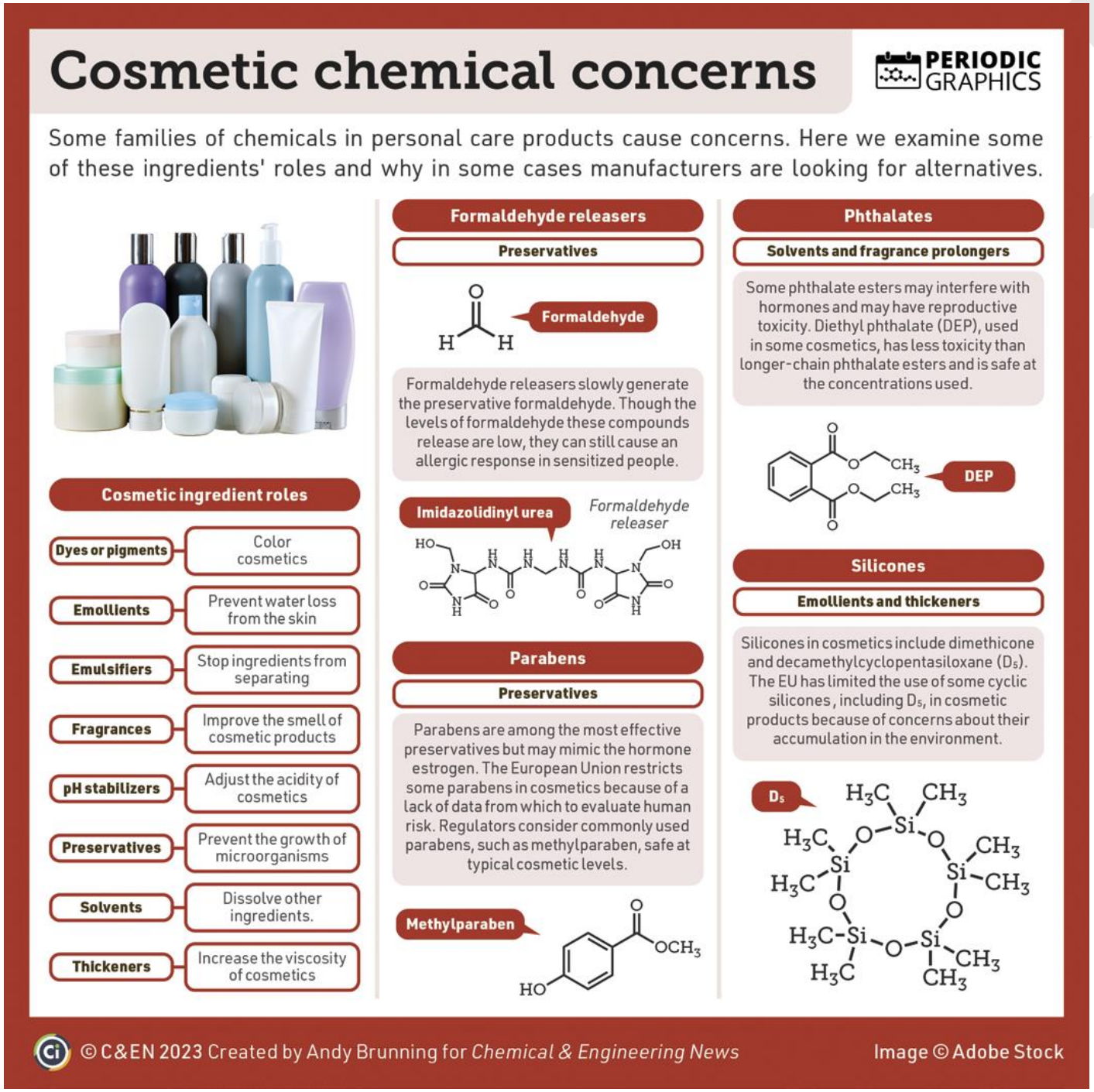


Discussion

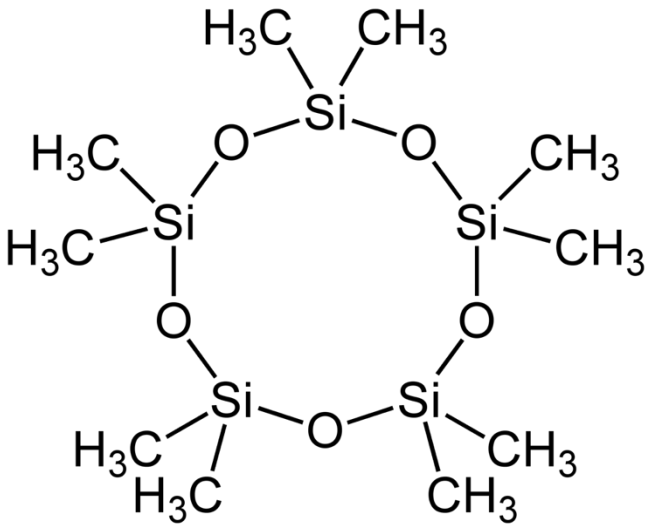
- Do we really need pesticides?
- How can we design even more benign pesticides?
- What can we do as consumers?
- How can governments support these efforts?

P2Science

The complexity of cosmetics

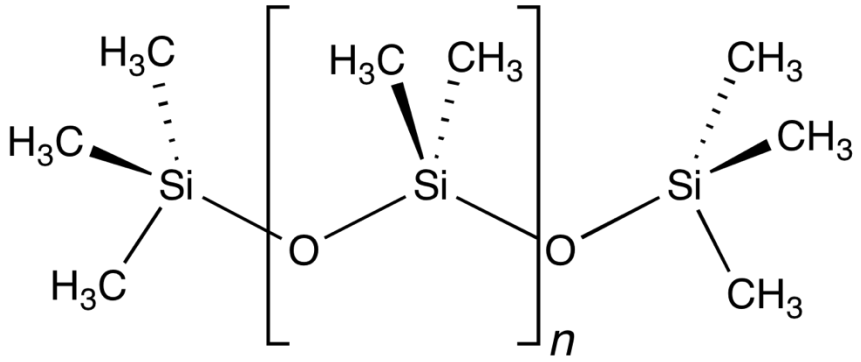


Silicones and emollients are problematic



Decamethylcyclopentasiloxane

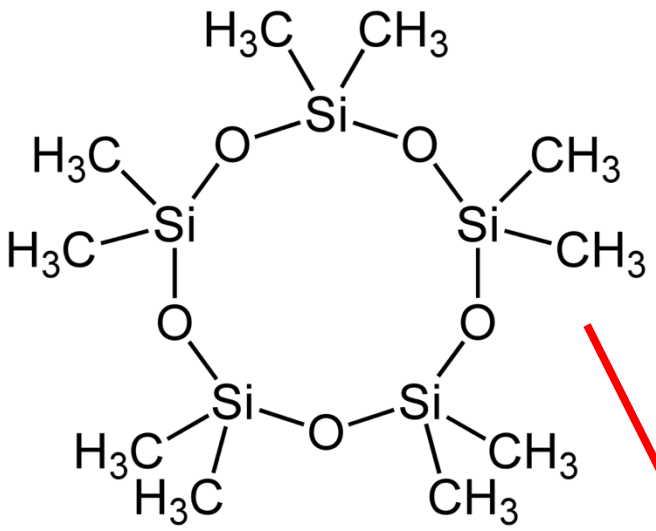
- volatile reagent used in deodorants for skin feel

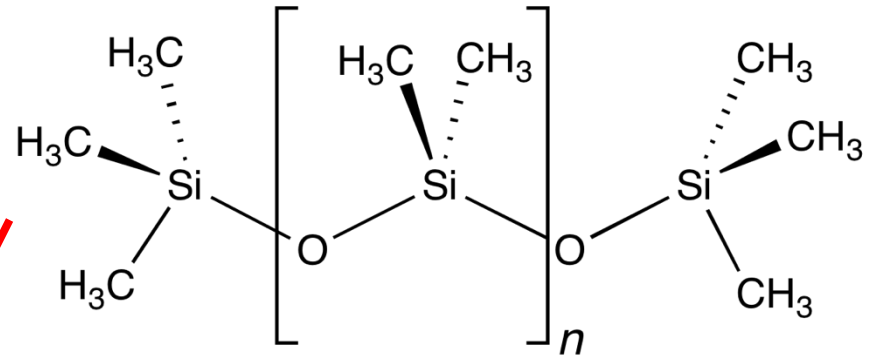


Polydimethylsiloxane/Dimethicones

- liquid additives often used in formulations of hair products

Silicones and emollients are problematic





Neither one was designed for degradability!
Both can cause problems for aquatic life.

Silicones and emollients are problematic

Most skincare and cosmetic products are ending up in the waterways and treatment plants sooner or later. This increases the price for water treatment dramatically, and also causes problems for the environment and our overal water quality.

P2's Approach

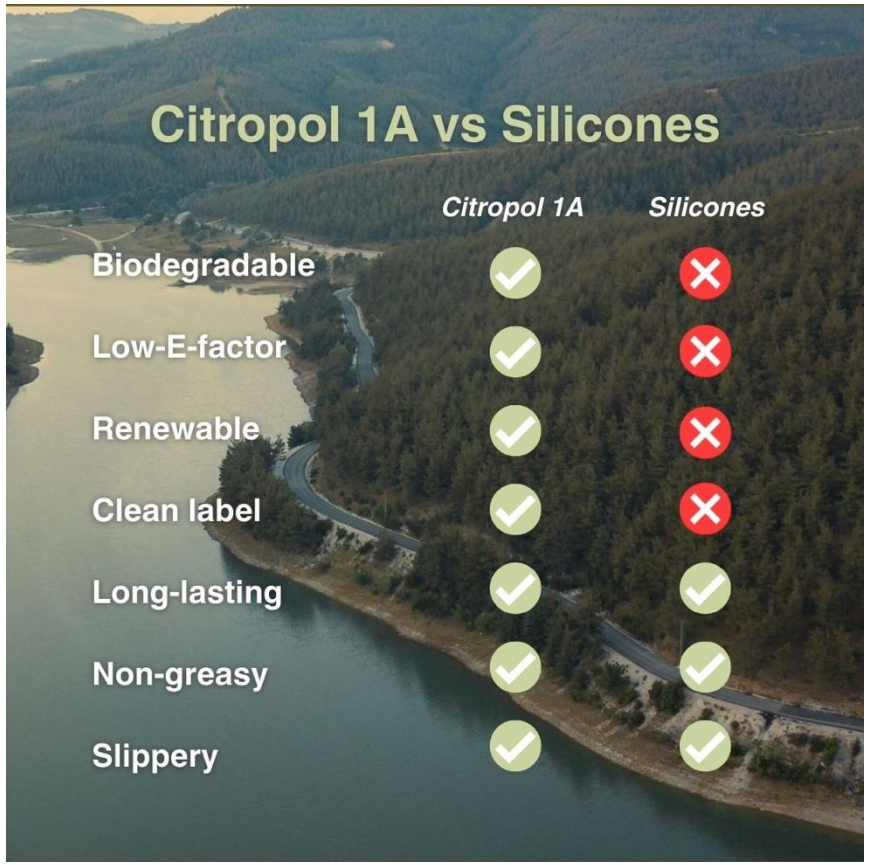
P2 Science uses chemistry to transform terpenes from the forest and oleochemicals from the field into safe, renewable, high performance, biodegradable, and multi-functional new ingredients for flavors, fragrances, cosmetics, personal care products, and specialty materials.

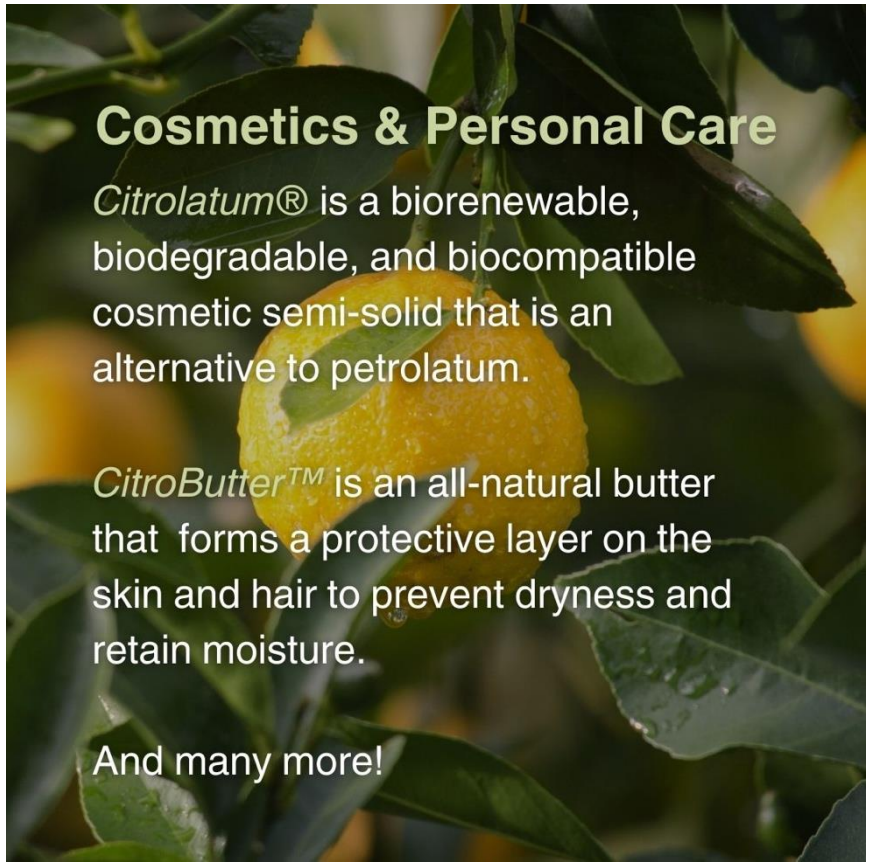
Citropol® is a flagship of P2 Science's products. It is a novel class of low MW liquid polymers that are made from 100% forest-derived terpenes through a clean, mild, and high yielding conversion process.

Citropol Based-Products

Terpene derived cosmetic products are superior to traditionally used silicones and significantly less harmful to the environment, especially water streams.

P2's Approach

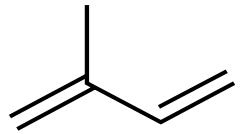




Important: these products are based on terpenes!

So what are terpenes?

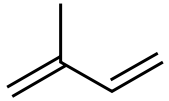
More than 30,000 terpenes exist, most of them are produced by plants, especially by conifers and citrics.
They are all based on **Isoprene**!



Isoprene

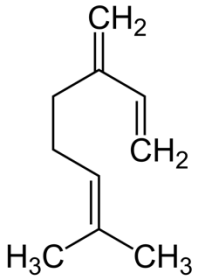
> 600 million tons of isporene are emitted by plants each year

So what are terpenes?

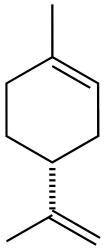


Isoprene

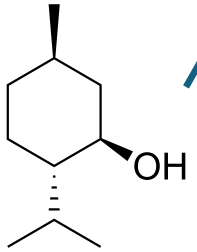
> 600 million tons of isporene are emitted by plants each year



Myrcene

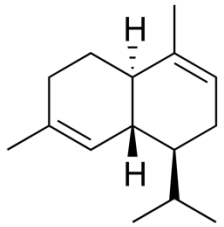


Menthol

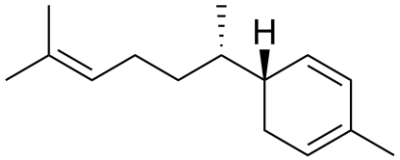


Limonene

Monoterpenes (n=2)

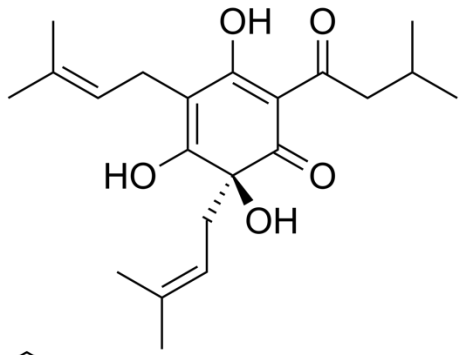


Cadinene

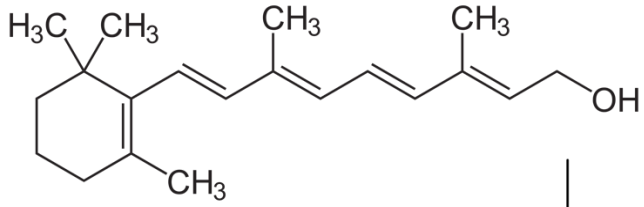


Zingiberene

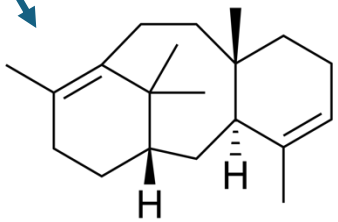
Sesquiterpenes (n=3)



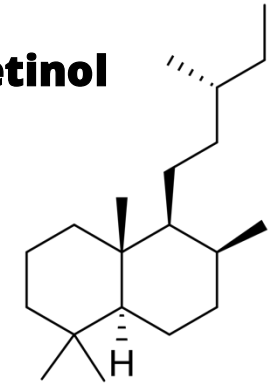
Humulone



Retinol



Taxadiene



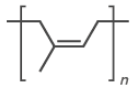
Labdane

Diterpenes (n=4)

And they are everywhere

Male condoms are commonly made from latex. To avoid latex allergies, polyurethane condoms can be used instead; polyisoprene condoms are also available. Female condoms are made from polyurethane or nitrile rubber.

1855



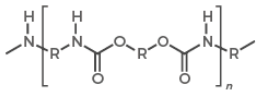
RUBBER

1920

A milky fluid mixture obtained from plants which contains rubber.

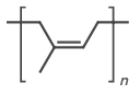
RUBBER LATEX

1994



POLYURETHANE

2008



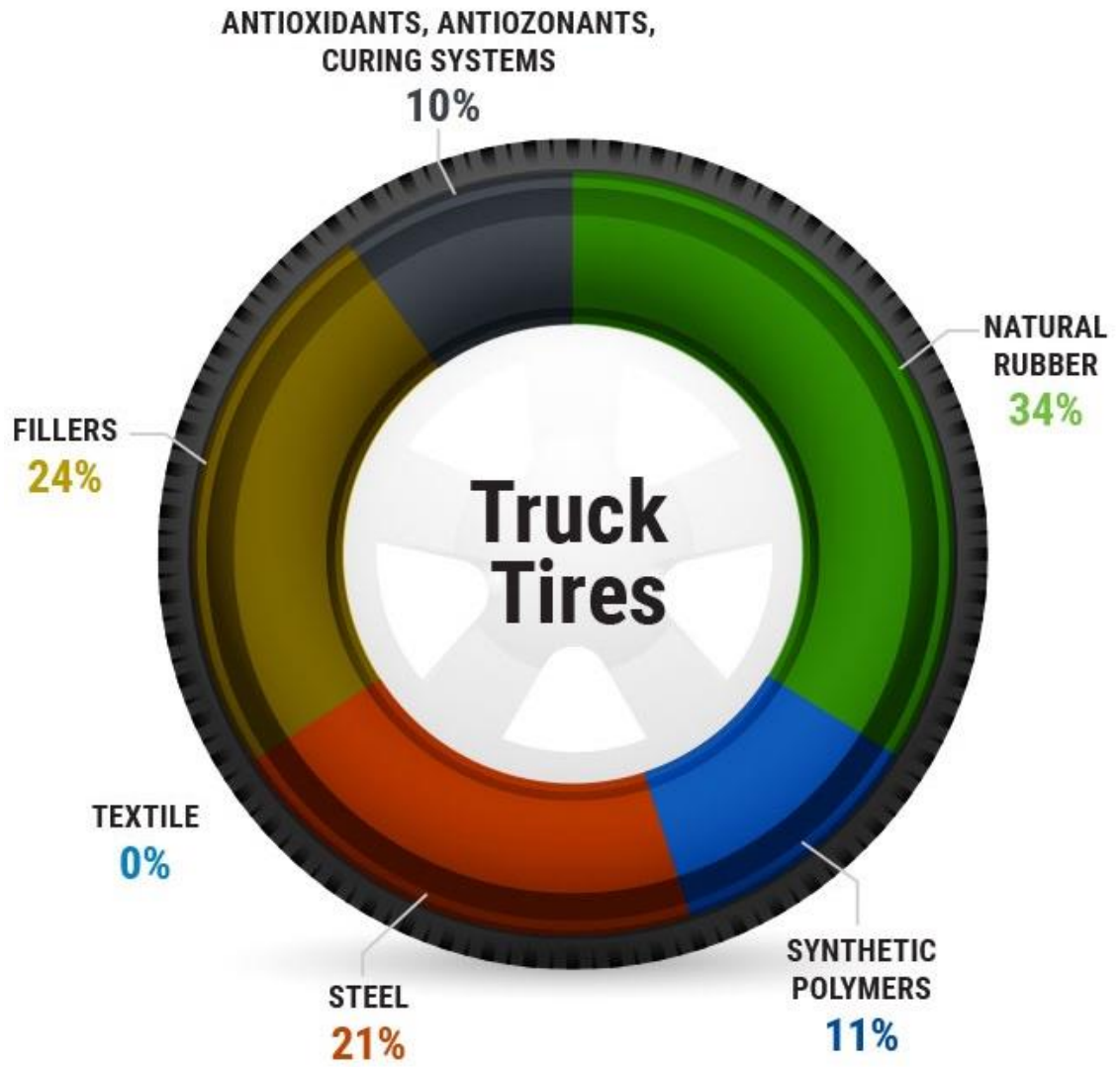
POLYISOPRENE

(synthetic rubber)

Condoms protect against both pregnancy and sexually transmitted diseases. Studies show that polyurethane condoms are slightly more prone to breakage than latex ones.

By PRA - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=9038298

And they are everywhere



https://www.ustires.org/whats-tire-0

P2 Science's: Process Intensification

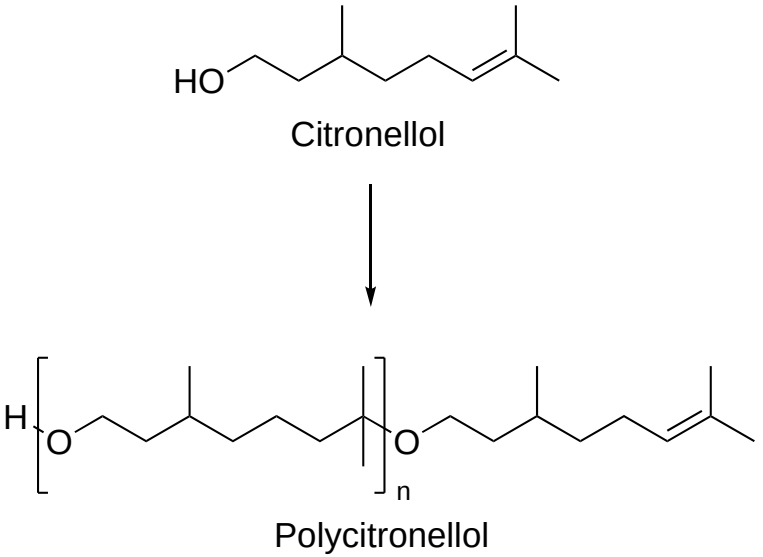
Although P2Science's processes are proprietary, they are based on the process intensification of terpene derivatizations.

Process Intensified Continuous Etherification (PICE™)

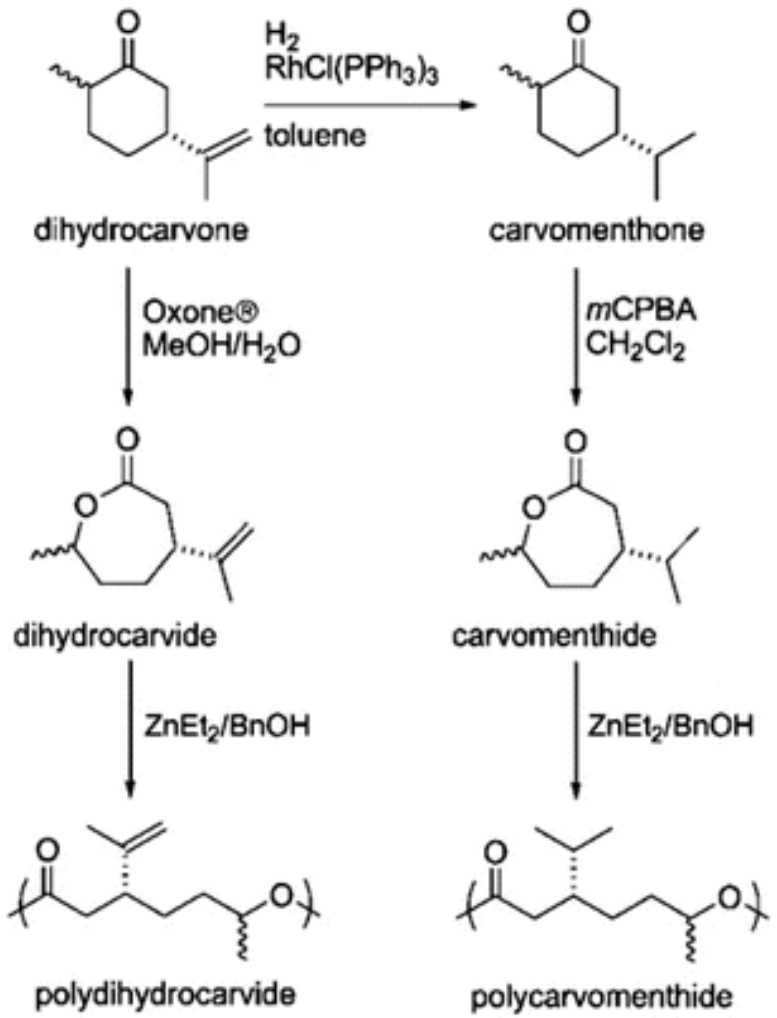
Process Intensified Ozonolysis (PIOz™)

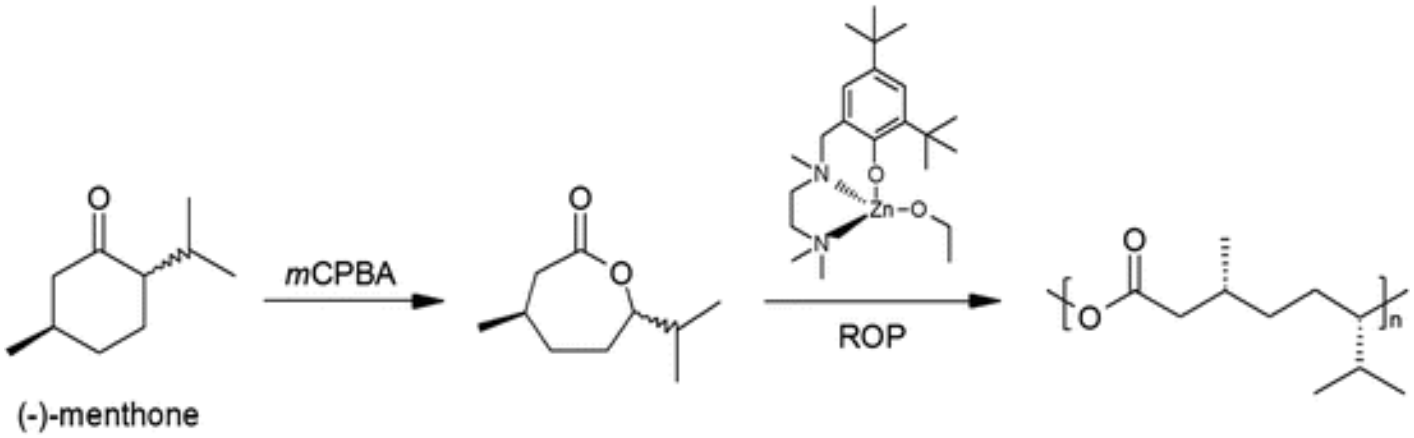
P2's Terpene-based polymers

Different grades of polymerization, *i.e.* different chain lengths, allow for the fine tuning of the mechanical and cosmetic properties.



Other terpene-based polymers





Zhao, J., Schlaad, H. (2011). Synthesis of Terpene-Based Polymers.

Discussion

- What other steps could make cosmetics more benign?
- Can you imagine other biological feedstocks?
- What the consumer do?
- What is important to consider to protect our waters?

Yale School of the Environment

Center for Green Chemistry & Green Engineering at Yale

- Advance Science
- Catalyze Implementation
- Prepare the next generation
- Raise Awareness

Thank You!

For questions, please reach out:

greenchemistry@yale.edu

https://www.globalgreenchem.com

https://www.chemistryforsustainability.org

https://greenchemistry.yale.edu/

@GREENCHEMISTRY.YALE

Executed by:

Center for Green Chemistry & Green Engineering at Yale

Implemented by:

UNIDO

Financed by:

gef global environment facility INVESTING IN OUR PLANET